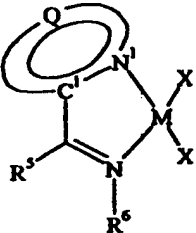




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<b>(21) International Application Number:</b> PCT/GB98/01205 <b>(22) International Filing Date:</b> 24 April 1998 (24.04.98)  <b>(30) Priority Data:</b> 9708487.5      25 April 1997 (25.04.97)      GB  <b>(71) Applicant (for all designated States except US):</b> BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BRES, Philippe-Luc [FR/GB]; 67 Corringway, Ealing, London W5 3HB (GB). GIBSON, Vernon, Charles [GB/GB]; Flat 2, 46 Prince's Gate, Exhibition Road, London SW7 2QA (GB). MA-BILLE, Christine, Daniele, Florence [FR/GB]; 108 Richmond Road, Kingston-upon-Thames, Surrey KT2 5EP (GB). REED, Warren [GB/GB]; 30 Kinross Drive, Sunbury-on-Thames, Middlesex TW16 7JU (GB). WASS, Duncan [GB/GB]; 31 Sweptstone Road, Heather, Coalville, Leicestershire LE67 2RE (GB). WEATHERHEAD, Richard, Henry [GB/GB]; 1 Cabbell Place, Addlestone, Surrey KT15 2XF (GB).		<b>(74) Agent:</b> PREECE, Michael; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).  <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> NOVEL COMPOUNDS AND THEIR USE IN POLYMERISATION  <b>(57) Abstract</b> <p>A nitrogen-containing metal complex compound having general formula (A) wherein the ring formed by Q, C<sup>1</sup> and N<sup>1</sup> is aromatically unsaturated, the divalent group Q comprises a chain of 3 or 4 atoms having the formula <math>-(CR)_n(Z)_r-</math> such that n is 2, 3 or 4; r is zero or 1; (n+r) = 3 or 4; Z is nitrogen, oxygen, or sulphur, M is nickel or palladium, the R groups can be, for example, hydrogen or hydrocarbyl, X is a univalent radical, for example, halide, hydride, hydrocarbyloxy. Q is preferably a pyridine ring. Also described is a catalyst for the polymerisation of 1-olefins comprising the defined metal complex and an activating quantity of a compound selected from organoaluminium compounds, alumoxanes and fluorohydrocarbylboron compounds.</p> <div style="text-align: right;">  <b>(A)</b> </div>		

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### **NOVEL COMPOUNDS AND THEIR USE IN POLYMERISATION**

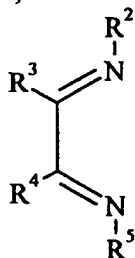
The present invention relates to novel transition metal compounds and to their use as polymerisation catalysts.

The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last twenty or thirty years, advances in the technology have lead to the development of Ziegler-Natta catalysts which have such high activities that that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent. Polymerisation of the monomers can be carried out in the gas phase (the "gas phase process"), for example by fluidising under polymerisation conditions a bed comprising the target polyolefin powder and particles of the desired catalyst using a fluidising gas stream comprising the gaseous monomer. In the so-called "solution process" the (co)polymerisation is conducted by introducing the monomer into a solution or suspension of the catalyst in a liquid hydrocarbon diluent under conditions of temperature and pressure such that the produced polyolefin forms as a solution in the hydrocarbon diluent. In the "slurry process" the temperature, pressure and choice of diluent are such that the produced polymer forms as a suspension in the liquid hydrocarbon diluent. These processes are generally operated at relatively

low pressures (for example 10-50 bar) and low temperature (for example 50 to 150°C).

Commodity polyethylenes are commercially produced in a variety of different types and grades. Homopolymerisation of ethylene with transition metal based catalysts leads to the production of so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (eg butene, hexene or octene) is employed commercially to provide a wide variety of copolymers differing in density and in other important physical properties. For example, copolymers made by copolymerising ethylene with higher 1-olefins using transition metal based catalysts have a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as "linear low density polyethylene" are in many respects similar to the so called "low density" polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

WO 96/23010 discloses a process for the polymerization of olefins, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of, inter alia,



with an olefin (for example ethylene) wherein the transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd;

R<sup>2</sup> and R<sup>5</sup> are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

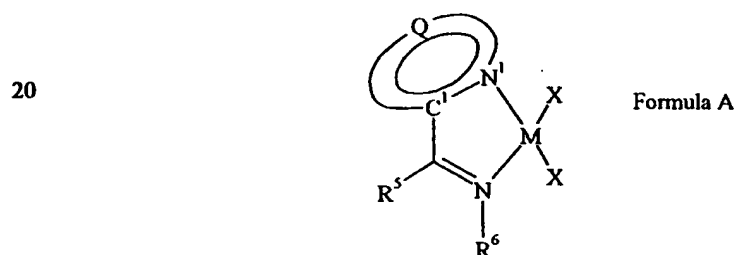
R<sup>3</sup> and R<sup>4</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R<sup>3</sup> and R<sup>4</sup> taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring; and provided that:

said transition metal also has bonded to it a ligand that may be displaced by said

olefin or add to said olefin.

An object of the present invention is to provide a novel catalyst suitable for polymerising olefins, and especially for polymerising ethylene alone or for copolymerising ethylene with higher 1-olefins. Throughout this specification  
 5 polymerisation is deemed to include any level of polymerisation from the production of low molecular weight products (eg dimers, trimers, tetramers, etc) through to ultra high molecular weight polymer. A further object of the invention is to provide an improved process for the polymerisation of olefins, especially of ethylene alone or the copolymerisation of ethylene with higher 1-olefins to provide  
 10 homopolymers and copolymers having controllable molecular weights. For example, using the catalyst of the present invention there can be made a wide variety of polyolefins such as, for example, liquid polyolefins, resinous or tacky polyolefins, solid polyolefins suitable for making flexible film and solid polyolefins having high stiffness. Catalysts of the present invention can be used to make linear  
 15 polyethylene free from, or substantially free from, chain branching.

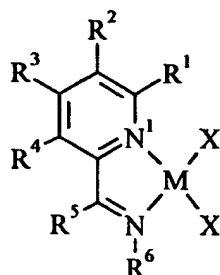
The present invention provides a nitrogen-containing metal complex compound having the general formula (Formula A):



25 wherein the ring formed by Q, C' and N' is aromatically unsaturated, the divalent group Q comprises a chain of 3 or 4 atoms having the formula  $-[(CR)_n(Z)_r]-$  such that n is 2, 3 or 4; r is zero or 1;  $(n+r) = 3$  or 4; Z is nitrogen, oxygen, or sulphur, C and C' are carbon, N and N' are nitrogen, M is nickel or palladium, the R groups attached to the carbon atoms in the chain are each independently selected from  
 30 hydrogen, halogen,  $C_{1-30}$  hydrocarbyl,  $NR^7_2$ ,  $OR^8$ , and  $NO_2$ ;  $R^7$  and  $R^8$  are each independently  $C_{1-30}$  hydrocarbyl, Z can occur within or at the end of the chain Q,  $R^5$  is hydrogen, halogen or a  $C_{1-30}$  hydrocarbyl or halohydrocarbyl group,  $R^6$  is hydrogen, halogen or a hydrocarbyl group having between 1 and 30 carbon atoms and each X is independently a univalent radical selected from halide, hydride,  
 35 hydrocarbyloxy, amide, hydrocarbyl, substituted hydrocarbyl,

heterohydrocarbyl, sulphur-containing organic or inorganic groups and oxygen-containing organic or inorganic groups. Suitable sulphur- and/or oxygen-containing organic or inorganic groups are for example, SR, OSO<sub>2</sub>R, OSO<sub>2</sub>CF<sub>3</sub>, OCOR wherein R is a hydrocarbyl group, for example a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group. Preferably each X is independently a univalent radical selected from halide, hydride, hydrocarbyloxy, amide, hydrocarbyl and substituted hydrocarbyl. The two X's can if desired be linked together, for example, by a hydrocarbyl bridge.

The ring formed by Q, C<sup>1</sup> and N<sup>1</sup> can, for example, be a pyrazole, pyridine, pyrazine, pyrimidine, thiazole or pyridine ring system, or can form part of a polynuclear heterocyclic system such as, for example, quinoline or indazole. Preferably the nitrogen-containing metal complex has the following formula (Formula A1) wherein the ring formed by Q, C and N<sup>1</sup> is a pyridine or substituted pyridine system;



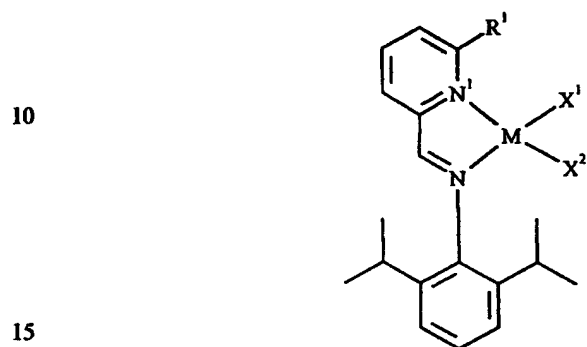
Formula A1

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> in the complex of Formula A1 are preferably hydrogen or hydrocarbyl groups containing 1 to 10 carbon atoms. Two or more of the groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> can themselves be linked together to form a further ring or rings, for example a benzene ring. Examples of these R groups are methyl, ethyl, n-propyl, n-butyl, n-hexyl, and n-octyl. Most preferably R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are all hydrogen atoms.

In the complex of Formula A and Formula A1, R<sup>5</sup> is preferably hydrogen or a hydrocarbyl or halohydrocarbyl group containing 1 to 10 carbon atoms. R<sup>6</sup> is preferably a substituted or unsubstituted aromatic group, for example, phenyl, 1-naphthyl, 2-naphthyl, 2-ethylphenyl, 2,6-diisopropylphenyl, and 2,6-di-n-butylphenyl, 2,6-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5-dichloro-2,6-diethylphenyl, and 2,6-bis(2,6-dimethylphenyl)phenyl.

The univalent radical X in the complex of Formula A and Formula A1 is preferably selected from halogen and hydrocarbyl groups. Examples of such groups are chloro, bromo, methyl, ethyl, n-propyl, isopropyl, n-butyl and n-octyl.

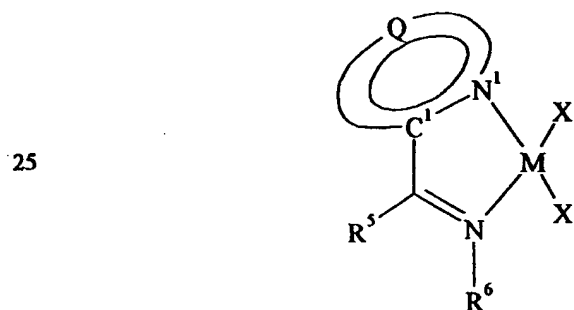
Preferred novel compounds of Formula A of the present invention are the compounds having the structural formula (Formula B) as follows:



Formula B

wherein R<sup>1</sup> is hydrogen or methyl, X<sup>1</sup> and X<sup>2</sup> are the same or different and are chlorine, bromine or methyl, and M is nickel or palladium.

The present invention further provides a catalyst for the polymerisation of 1-olefins comprising (1) the compound of Formula A:



Formula A

and (2) an activating quantity of a compound selected from organoaluminium compounds, alumoxanes and fluorohydrocarbylboron compounds.

Q, R<sup>5</sup>, R<sup>6</sup>, M and X symbolise the same groups and atoms as described above, and the preferences stated above in relation to the compounds of formula A A1 and B apply equally to the preferred catalyst of the present invention.

Suitable organoaluminium compounds include trialkylaluminium

compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, and diethylaluminium chloride.

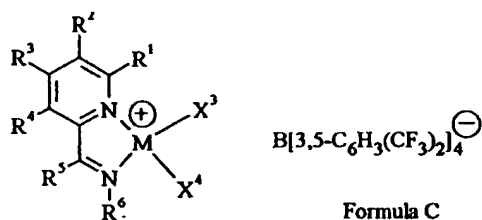
Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula  $[R^9AlO]_s$  and the linear alumoxanes by the formula  $R^{10}(R^{11}AlO)_s$  wherein  $s$  is a number from about 2 to 50, and wherein  $R^9$ ,  $R^{10}$ , and  $R^{11}$  represent hydrocarbyl groups, preferably  $C_1$  to  $C_6$  alkyl groups, for example methyl, ethyl or butyl groups.

Examples of suitable fluorohydrocarbylboron compounds are dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate,  $H^+(OEt_2)[(bis-3,5-trifluoromethyl)phenyl]borate$ , trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

In the preparation of the catalyst of the present invention the quantity of activating compound selected from organoaluminium compounds, alumoxanes and fluorohydrocarbylboron compounds to be employed in the catalyst of the present invention is easily determined by simple testing, for example by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. When it is desired to use an alumoxane activator, it is generally found that the quantity employed is sufficient to provide 1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium per Ni or Pd metal atom in the compound of Formula A.

When the metal complexes of the present invention are activated to form a catalyst in accordance with the present invention using the compound  $H(Et_2O)_2B[3,5-C_6H_3(CF_3)_2]_4$  it has been found that clearly defined catalytically active ionic species are produced. Accordingly the present invention further provides a catalytically active ionic species having the general formula:

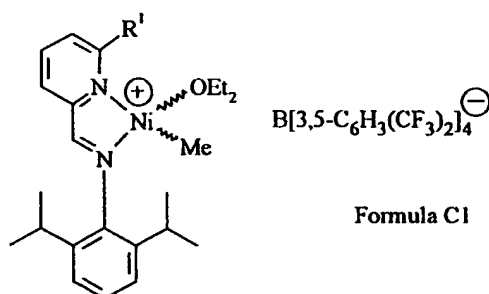




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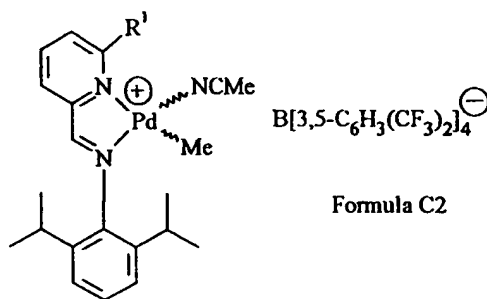
wherein  $R^1$  to  $R^6$  are as defined above, and  $X^3$  is selected from hydrocarbonyl groups, for example, methyl, ethyl, propyl or benzyl, and  $X^4$  is selected from neutral electron donating ligands, for example ethers such as diethyl ether, nitriles such as acetonitrile. Examples of particular catalytically active ionic species in accordance with the present invention include the following compounds (Formula C1 and C2):

15



20 and

25



wherein  $R^1$  in each of these formulae is preferably hydrogen or methyl.

The catalyst of the present invention is preferably supported on a support material, for example, silica, alumina, zirconia, or on a polymer or a prepolymer, for example polyethylene or polystyrene. Formation of the supported catalyst can be achieved for example by treating the compound of Formula A with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurrying a particulate support material with the product and evaporating the volatile diluent.

The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the Formula A compound.

The present invention further provides a process for the polymerisation and copolymerisation of polymerisable monomeric material, preferably one or more 1-olefins, comprising contacting the monomeric material under polymerisation conditions with the catalyst of the present invention.

The polymerisation conditions can be, for example, solution phase, slurry phase or gas phase. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised bed conditions. Suitable monomers for use in the polymerisation process of the present invention are, for example, ethylene, propylene, butene, hexene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Preferred monomers for homopolymerisation processes are ethylene and propylene. The catalyst can be used for copolymerising ethylene with other 1-olefins such as propylene, 1-butene, 1-hexene, 4-methylpentene-1, and octene.

Methods for operating the gas phase fluidised bed process for making polyethylene and ethylene copolymers are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidising gas stream through the bed. The fluidising gas circulating through the bed serves to remove the heat of polymerisation from the bed and to supply monomer for polymerisation in the bed. Thus the fluidising gas generally comprises the monomer(s) normally together with some inert gas (eg nitrogen) and optionally with hydrogen as molecular weight modifier. The hot fluidising gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerisation. Catalyst is preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises fluidisable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerisation of the monomer(s). Preferably means are provided to discharge polymer from the bed continuously or at regular

intervals to maintain the fluidised bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 bars, and at temperatures for example, between 50 and 120 °C. The temperature of the bed is maintained below the sintering temperature of the fluidised polymer to avoid problems of agglomeration.

In the gas phase fluidised bed process for polymerisation of olefins it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed or recycling a condensed volatile liquid to the bed under conditions such that the liquid provides a cooling effect by evaporating in the bed (thereby absorbing additional heat of polymerisation from the bed by the "latent heat of evaporation" effect). When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out and can be separated and sprayed into the bed, or recycled to the bed with the recycle gas. Such techniques are described, for example, in EP-A-89691, EP-A-699212, EP-A-784637, EP-A-696293 and EP-A-784638 and in our US Patent 5541270 which are hereby incorporated in this specification by reference. It is preferred to reintroduce the condensed liquid into the bed using the process described in our US Patent 5541270.

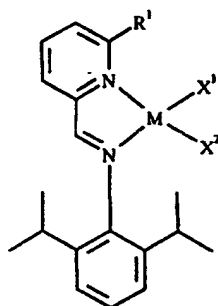
The present invention is illustrated in the following Examples.

#### EXAMPLES

Examples 1 to 5 illustrate the preparation of novel nickel and palladium nitrogen-containing complex compounds in accordance with the present invention. Examples 6 to 12 illustrate polymerisation of ethylene using catalysts prepared from these complexes. Example 13 illustrates the preparation of two pyrazine complexes in accordance with the present invention and Example 14 shows the polymerisation activity of these complexes. All manipulations of compounds sensitive to air and/or moisture were performed using a conventional vacuum/inert atmosphere (N<sub>2</sub>) glove-box. All solvents employed were carefully dried using conventional techniques.

In Examples 1 to 5 metal complex compounds were prepared having the general formula:

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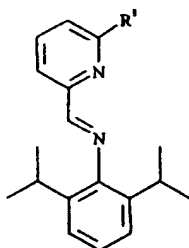
General Formula for Metal  
Complexes 1 to 5  
prepared in Examples 1 to 5

- 10 In Metal Complex-1,  $M = \text{Ni}$ ,  $R^1 = \text{H}$ ,  $X^1$  and  $X^2$  are both Br.  
 In Metal Complex-2,  $M = \text{Ni}$ ,  $R^1 = \text{methyl}$ ,  $X^1$  and  $X^2$  are both Br.  
 In Metal Complex-3,  $M = \text{Ni}$ ,  $R^1 = \text{H}$ ,  $X^1$  and  $X^2$  are both methyl.  
 In Metal Complex-4,  $M = \text{Pd}$ ,  $R^1 = \text{H}$ ,  $X^1 = \text{Cl}$ ,  $X^2 = \text{methyl}$ .  
 In Metal Complex-5,  $M = \text{Pd}$ ,  $R^1 = \text{methyl}$ ,  $X^1 = \text{Cl}$ ,  $X^2 = \text{methyl}$ .

15

The preparation of these metal complexes was carried out using the following intermediate compounds:

20



Intermediate 1:  $R^1 = \text{Hydrogen}$   
 Intermediate 2:  $R^1 = \text{Methyl}$

25

These intermediate compounds were prepared using the method described by M Weidenbruch, H. Pied, A. Lesch, K. Peters and H.G. von Schnering in Journal of Organometallic Chemistry, 1993, 454, 35.

#### Example 1

30

Preparation of Metal Complex-1. Methylene chloride (30 ml) was added to a mixture of "Intermediate 1" (0.45g, 1.7 mmol) and (dme)NiBr<sub>2</sub> (0.50g, 1.62 mmol) in a Schlenk vessel. The compound "(dme)" is 1,2-dimethoxyethane. The mixture was stirred for 18 hours during which time an orange precipitate was formed. This precipitate was isolated by filtration, washed with three aliquots (each of 10ml) of diethyl ether and dried in vacuo for 1 hour. The yield of Metal

35

Complex-1 was 0.50g (64% of theoretical).

**Example 2**

Preparation of Metal Complex-2. Methylene chloride (30 ml) was added to a mixture of "Intermediate 2" (0.80g, 2.80 mmol) and (dme)NiBr<sub>2</sub> (0.70g, 2.27 mmol) in a Schlenk vessel. The mixture was stirred for 18 hours during which time an orange solution formed. Solvent was removed under reduced pressure and the resultant pale orange powder was washed with three aliquots (each of 10ml) of diethyl ether and dried in vacuo for 1 hour. The yield of Metal Complex-2 was 0.67g (60% of theoretical).

**Example 3**

Preparation of Metal Complex-3. Methyl magnesium bromide (0.5 ml of a 3.0 molar solution in diethylether, 1.5 mmol) was added dropwise to a stirred suspension of Metal Complex-1 (0.36g, 0.74 mmol), the latter being prepared as described in Example 1, at -30°C. This mixture was stirred for 2 hours during which time the solution was allowed to warm to 0°C. The solution became a deep blue-green colour. 1,4-dioxane (5ml) was added and a fine precipitate formed. The solution was filtered and solvent removed under reduced pressure. The resultant solid was washed with three 10 ml aliquots of pentane to yield 0.18g (70% of theoretical) of Metal Complex-3 as a fine dark green powder.

**Example 4**

Preparation of Metal Complex-4. Methylene chloride (30 ml) was added to a mixture of "Intermediate 1" (0.20 g, 0.75 mmol) and (COD)PdMeCl (0.20 g, 0.75 mmol) in a Schlenk vessel. "(COD)" is cyclooctadiene. The mixture was stirred at room temperature for 18 hrs during which time a yellow/orange precipitate formed. This precipitate was isolated by filtration, washed with three 10 ml aliquots of Et<sub>2</sub>O then dried in vacuo for 1 hr. Yield of Metal Complex-4 was 0.25 g (79 % of theoretical).

**Example 5**

Preparation of Metal Complex-5. Methylene chloride (30 ml) was added to a mixture of "Intermediate 2" (0.22 g, 0.77 mmol) and (COD)PdMeCl (0.20 g, 0.75 mmol) in a Schlenk vessel. The mixture was stirred for 18 hrs during which time an orange solution formed. Solvent was removed under reduced pressure and the resultant pale orange powder washed with three 10 ml aliquots of Et<sub>2</sub>O and dried in vacuo for 1 hr. Yield Metal Complex-5 was 0.25 g, (75 % of theoretical)

**Example 6**

Polymerisation of ethylene using a catalyst prepared from Metal Complex-1 (see Example 1).

A 10% solution of methylalumoxane (MAO) in toluene (1.4 ml, 2.0 mmol, 200 equivalents) was added via syringe to a stirred suspension of Metal Complex-1 (4.8 mg, 0.01 mmol) in 50 ml toluene. The methylalumoxane solution is commercially available from Aldrich. The produced catalyst solution was degassed under reduced pressure and back-filled with an atmosphere of ethylene. Fuming was observed and the solution became hot almost immediately. During the run time of 30 minutes the solution was left open to a supply of ethylene at one atmosphere and stirred vigorously at 25°C. The polymerisation was terminated by the addition of dilute HCl (ca. 100 ml) and then stirred for 30 minutes to dissolve MAO residues. The organic layer was separated, dried over MgSO<sub>4</sub>, and the solvent removed under reduced pressure. After drying in vacuo overnight, the polyethylene product was isolated as a viscous, waxy oil. Yield 3.46 g. Activity was 690 g mmol<sup>-1</sup>hr<sup>-1</sup>bar<sup>-1</sup>.

**Example 7**

Polymerisation of ethylene using a catalyst prepared from Metal Complex-2 (see Example 2).

Preparation of the catalyst and polymerisation of ethylene were carried out substantially as described in Example 6 except that the catalyst was prepared from Metal Complex-2 (5.0 mg, 0.01 mmol) and MAO solution (1.4 ml, 2.0 mmol, 200 equivalents). The run time of 30 minutes. Polyethylene was isolated as a viscous oil. Yield was 0.20 g. Activity was 41 g mmol<sup>-1</sup>hr<sup>-1</sup>bar<sup>-1</sup>.

**Example 8**

Polymerisation of ethylene using a catalyst prepared from Metal Complex-3 (see Example 3).

Diethylether (10 ml) was added to Metal Complex-3 (17.8 mg, 0.05 mmol) and H(Et<sub>2</sub>O)<sub>2</sub>B[3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (50.6 mg, 0.05 mmol) at 0°C in a Schlenk vessel. A dark red solution formed almost immediately which was stirred for ca. 5 minutes. After this time solvent was removed under reduced pressure to yield the active catalyst as a dark red solid.

All of this dark red solid product (64 mg, 0.05 mmol assuming 100% yield was obtained) was dissolved in methylene chloride (30 ml). This solution was degassed under reduced pressure and back-filled with an atmosphere of ethylene.

During the run time of 1 hour the solution was left open to a supply of ethylene at one atmosphere pressure and stirred vigorously at 0°C. The polymerisation was terminated by the addition of dilute HCl (ca. 100 ml) and then stirred for 1 hr to dissolve metal residues. The organic layer was separated, dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. After drying in vacuo overnight, polyethylene was isolated as a colourless, free flowing oil. The yield was 8.25 g, corresponding to an activity of 165 g mmol<sup>-1</sup>hr<sup>-1</sup>bar<sup>-1</sup>.

#### **Example 9**

Polymerisation of ethylene using a catalyst prepared from Metal Complex-4 (see Example 4).

Acetonitrile (20 ml) was added to a mixture of Metal Complex-4 (0.10 g, 0.24 mmol) and NaB(3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (0.21g, 0.24 mmol) at room temperature and stirred for about 20 minutes. After this time the solution was filtered and solvent removed under reduced pressure to yield a catalytically active yellow crystalline solid. Yield 0.25 g, 85 % of theoretical.

This catalyst (50 mg, 0.04 mmol) was used to polymerise ethylene substantially as described in Example 8, except that the run time was 18 hours at 25°C.

Polyethylene was isolated as a free-flowing yellow oil. The yield was 0.24 g, corresponding to an activity of 0.3 g mmol<sup>-1</sup>hr<sup>-1</sup>bar<sup>-1</sup>.

#### **Example 10**

Polymerisation of ethylene using a catalyst prepared from Metal Complex-5 (see Example 5).

MeCN (20 ml) was added to a mixture of Metal Complex-5 (0.05 g, 0.11 mmol) and NaB[3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (0.10 g, 0.11 mmol) at room temperature and stirred for about 20 minutes. After this time the solution was filtered and solvent removed under reduced pressure to yield a catalytically active yellow/orange glassy solid.

The yield was 0.12 g, corresponding to 80 % of theoretical.

This catalyst (52 mg, 0.04 mmol) was used to polymerise ethylene as described in Example 9. Polyethylene was isolated as a free-flowing yellow oil. The yield was 0.07g, corresponding to an activity of 0.1 g mmol<sup>-1</sup>hr<sup>-1</sup>bar<sup>-1</sup>.

#### **Example 11**

Polymerisation of ethylene using a catalyst prepared from Metal Complex-1 (nickel bromide complex of the pyridylimine compound - see Example 1).

Polymerisation was carried out in a 300ml polymerisation vessel fitted with a stirrer. The polymerisation vessel was purged with dry nitrogen. The catalyst was

prepared from Metal Complex-1 (8.12  $\mu$ mol) dissolved in toluene and sufficient methylalumoxane in toluene solution (Aldrich) to provide a MAO/Metal Complex ratio of 520. This provided a polymerisation medium containing 0.0393mg catalyst (based on the weight of Metal Complex-1) per ml of toluene. The polymerisation was carried out at 50°C under a pressure of 3 bar ethylene for 1h50mins. The polyethylene product was isolated and dried substantially as described in Example 6. The yield of polyethylene was 0.10 gram. The polyethylene had the following properties:  $M_w = 948,000$ ;  $M_n = 447,000$ ; polydispersity ( $M_w/M_n$ ) = 2.1. The polyethylene was substantially linear as determined by NMR analysis (see foot of Table following Example 12).

### Example 12

Polymerisation of ethylene using a catalyst prepared from Metal Complex-5 (Palladium methylchloride complex of the methylpyridylimine compound - see Example 5).

A series of three polymerisation Runs was carried out in toluene on a 1 litre scale using a stirred polymerisation vessel. The catalyst was activated using MAO in each case, and increasing the amount as the Runs progressed. Polymerisation was carried out under an ethylene pressure of 10 bar in Run 12.1. In Runs 12.2 and 12.3 the pressure was 10 bar initially, increasing to 20 bar as the Run progressed. The following Table shows the Run polymerisation times and temperature, yield of polyethylene and the polymer properties.

Run	Time	Temp. (°C)	Yield (g)	$M_w \times 10^6$	$M_n \times 10^6$	$M_w/M_n$	Notes
12.1	4h5min	25	24.44	1.601	0.759	2.1	(1)
12.2	2h43min	50	63.66	0.742	0.287	2.6	(2)
12.3	3h	75	31.47	0.735	0.361	2.0	(2)

### Notes on the Table:

- (1) Polyethylene was virtually free from branching; (Me 0.5 per 1000)/chain ends (by NMR - see below).
- (2) Polyethylene was virtually free from branching (by NMR - see below).  $C^{13}$  NMR run on samples as solutions in  $C_2D_2Cl_4$ /1,2,4-trichlorobenzene at 130 °C showed them to be essentially linear polyethylenes with no significant branching or chain ends. High MW was confirmed by GPC.

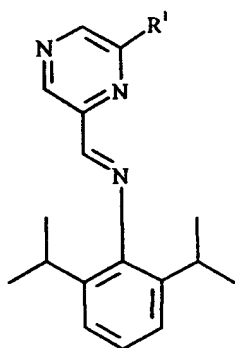
### Example 13

13.1 Synthesis of Metal Complex-13.1 (see structural formula below)



"Intermediate 3" was prepared as follows: A discrete mixture of 2,6-diisopropylaniline (1.6g, 9.2 mmol) and 2-pyrazinecarboxaldehyde (1.0g, 9.2 mmol) was heated to ca. 100°C and stirred at this temperature for 15 minutes.

- 5 Crystallisation of the crude reaction mixture from cold pentane or distillation yielded pure "Intermediate-3" as a yellow solid. 2-Pyrazinecarboxaldehyde was synthesised according to the procedure of H Rutner and P.E Spoerri in the Journal of Organic Chemistry, 1968, 28, 1898 from the commercially available 2-pyrazine carboxylic acid. Methylene chloride ( ca. 30 ml) was added to a mixture
- 10 of "Intermediate 3" (0.45g, 1.7 mmol) and (dme)NiBr<sub>2</sub> (0.50g, 1.62 mmol) in a Schlenk vessel. The compound "(dme)" is 1,2-dimethoxyethane. The mixture was stirred for 18 hours during which time an orange precipitate was formed. This precipitate was isolated by filtration, washed with three aliquots (each of 10ml) of diethyl ether and dried in vacuo for 1 hour. The yield of Metal Complex-13.1 was
- 15 0.5g (75% of theoretical).

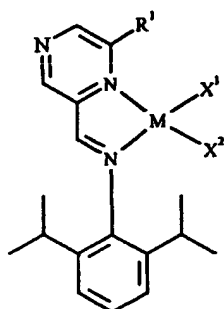


Intermediate 3

### 13.2 Synthesis of Metal Complex-13.2 (see structural formula below)

- Methyl magnesium bromide (0.5 ml of a 3.0 molar solution in diethylether, 1.5 mmol) was added dropwise to a stirred suspension of Metal Complex 13.1 (0.36g, 0.74 mmol) in Et<sub>2</sub>O at -30°C. This mixture was stirred for 2 hours during
- 30 which time the solution was allowed to warm to 0°C. After this time the solution became a deep blue-green colour. 1,4-dioxane (5ml) was added and a fine precipitate formed. The solution was filtered and solvent removed under reduced pressure. The resultant solid was washed with three 10 ml aliquots of pentane to
- 35 yield 0.18g (70% of theoretical) of Metal Complex-13.2 as a fine dark green

powder.



General Formula for Metal Complexes 13.1 and 13.2 prepared in Examples 13

In Metal Complex-13.1  $M = \text{Ni}$ ,  $R^1 = \text{H}$ ,  $X^1$  and  $X^2$  are both bromide.

In Metal Complex-13.2  $M = \text{Ni}$ ,  $R^1 = \text{H}$ ,  $X^1$  and  $X^2$  are both methyl.

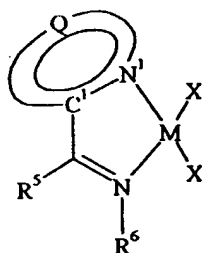
#### Example 14 - Polymerisation Tests

$\text{Et}_2\text{O}$  (ca. 10ml) was added to Metal Complex-13.2 (17.8mg, 0.05 mmol) and  $\text{H}(\text{Et}_2\text{O})_2\text{B}[3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2]_4$  (50.6 mg, 0.05 mmol) at  $0^\circ\text{C}$  in a Schlenk vessel. A dark red solution formed almost immediately which was stirred for ca. 5 minutes.

After this time solvent was removed under reduced pressure to yield the active catalyst as a dark red solid. All of this dark red solid product (64 mg, 0.05 mmol assuming 100% yield was obtained) was dissolved in methylene chloride (ca. 30 ml). This solution was degassed under reduced pressure and back-filled with an atmosphere of ethylene. During the run time of 1 hour the solution was left open to a supply of ethylene at one atmosphere pressure and stirred vigorously at  $0^\circ\text{C}$ . The polymerisation was terminated by the addition of dilute  $\text{HCl}$  (ca. 100 ml) and then stirred for 1 hr to dissolve metal residues. The organic layer was separated, dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure. After drying in vacuo overnight, polyethylene was isolated as a white solid. The yield was 5.0 g. corresponding to an activity of  $100 \text{ g mmol}^{-1}\text{hr}^{-1}\text{bar}^{-1}$ . The polyethylene was found to be of higher average molecular weight than the material obtained in Example 8. The Polymerisation Test of Example 14 was repeated using the Metal Complex-13.1 instead of Metal Complex-13.2 and MAO activator instead of the fluorohydrocarbyl boron compound. Some polyethylene was produced, but this catalyst was considerably less active than that obtained using Metal Complex-13.2.

## Claims:

1. A nitrogen-containing metal complex compound having the general formula (Formula A):



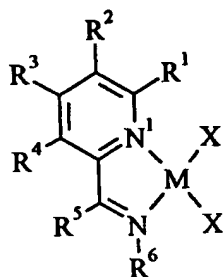
Formula A

- 10 wherein the ring formed by Q, C<sup>1</sup> and N<sup>1</sup> is aromatically unsaturated, the divalent group Q comprises a chain of 3 or 4 atoms having the formula  $-(\text{CR})_n(\text{Z})_r-$  such that n is 2, 3 or 4; r is zero or 1;  $(n+r) = 3$  or 4; Z is nitrogen, oxygen, or sulphur, C and C<sup>1</sup> are carbon, N and N<sup>1</sup> are nitrogen, M is nickel or palladium, the R groups attached to the carbon atoms in the chain are each independently selected from
- 15 hydrogen, halogen, C<sub>1-30</sub> hydrocarbyl, NR<sup>7</sup>, OR<sup>8</sup>, and NO<sub>2</sub>; R<sup>7</sup> and R<sup>8</sup> are each independently C<sub>1-30</sub> hydrocarbyl, Z can occur within or at the end of the chain Q, R<sup>5</sup> is hydrogen, halogen or a C<sub>1-30</sub> hydrocarbyl or halohydrocarbyl group, R<sup>6</sup> is hydrogen, halogen or a hydrocarbyl group having between 1 and 30 carbon atoms and each X is independently a univalent radical selected from halide, hydride,
- 20 hydrocarbyloxy, amide, hydrocarbyl and substituted hydrocarbyl, heterohydrocarbyl, sulphur-containing organic or inorganic groups and oxygen-containing organic or inorganic groups.
2. A complex as claimed in Claim 1 wherein each X is independently a
- 25 hydrocarbyl and substituted hydrocarbyl.

3. A complex as claimed in Claim 1 or 2 wherein the ring formed by Q, C and N<sup>1</sup> is a pyrazole, pyridine, pyrazine, pyrimidine, thiazole or pyridine ring system, or forms part of a polynuclear heterocyclic system.

4. A complex as claimed in Claim 1, 2 or 3 having the formula (Formula A1);

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Formula A1

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wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are hydrogen or hydrocarbyl groups containing 1 to 10 carbon atoms, and two or more of the groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> can themselves be linked together to form a further ring or rings.

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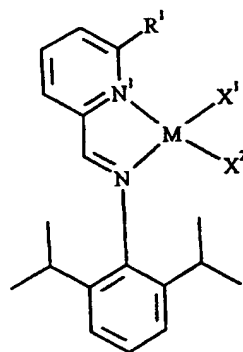
5. A complex as claimed in any one of the preceding Claims wherein R<sup>5</sup> is hydrogen or a hydrocarbyl or halohydrocarbyl group containing 1 to 10 carbon atoms and R<sup>6</sup> is a substituted or unsubstituted aromatic group.

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6. A complex as claimed in any one of the preceding Claims wherein the univalent radical X is selected from chloro, bromo, methyl, ethyl, n-propyl, isopropyl, n-butyl and n-octyl.

7. A complex as claimed in any one of the preceding Claims having the structural formula (Formula B):

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Formula B

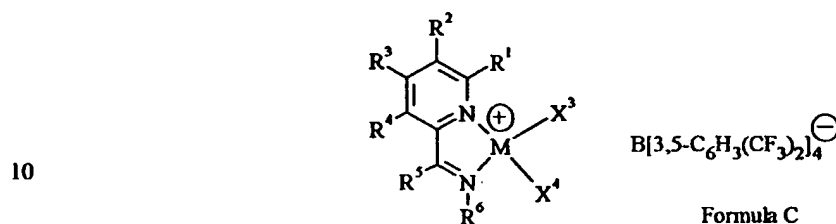
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wherein R<sup>1</sup> is hydrogen or methyl, X<sup>1</sup> and X<sup>2</sup> are the same or different and are chlorine, bromine or methyl.

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8. A catalyst for the polymerisation of 1-olefins comprising (1) the complex compound claimed in any one of the preceding Claims and (2) an activating quantity of a compound selected from organoaluminium compounds, alumoxanes and fluorohydrocarbylboron compounds.

5 9. A catalytically active ionic species having the general formula (Formula C):



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrogen or hydrocarbyl groups containing 1 to 10 carbon atoms, and two or more of the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  can themselves be linked together to form a further ring or rings,  $R^5$  is hydrogen, halogen or a  $C_{1-30}$  hydrocarbyl or halohydrocarbyl group,  $R^6$  is hydrogen, halogen or a hydrocarbyl group having between 1 and 30 carbon atoms,  $X^3$  is selected from hydrocarbyl groups, and  $X^4$  is selected from neutral electron donating ligands.

10 10. A catalytically active ionic species as claimed in Claim 9 wherein  $R^5$  is methyl, ethyl, propyl or benzyl and  $R^6$  is selected from ethers and nitriles.

11. A catalyst as claimed in Claim 8 or a catalytically active species as claimed in Claim 9 or 10 supported on a support material selected from silica, alumina, zirconia, or a polymer or a prepolymer.

25 12. A process for the polymerisation and copolymerisation of polymerisable monomeric material comprising contacting the monomeric material under polymerisation conditions with the catalyst or catalytically active species claimed in any one of Claims 8 to 11.

13 A process as claimed in Claim 12 wherein the polymerisation is carried out under slurry, solution or gas phase polymerisation conditions.

14. A process as claimed in Claim 12 or 13 wherein the monomeric material comprises ethylene or propylene, or a mixture of ethylene with propylene, 1-butene, 1-hexene, 4-methylpentene-1 or octene.

15. A process as claimed in any one of Claims 12 to 14 wherein the polymerisation is carried out in the gas phase and comprising feeding a volatile

liquid or recycling a condensed volatile liquid to the bed provide a cooling effect.

16. Olefin polymer prepared by the process claimed in any one of Claims 12 to 15.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01205

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C08F4/70 C08F4/80 C07F15/00 C07F15/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 02298 A (DU PONT ; JOHNSON LYNDAY KAYE (US); FELDMAN JERALD (US); KREUTZER KR) 23 January 1997 see page 53; example 99 see page 54; figure 106	1-8, 12-14, 16
Y	see page 30, line 5 - line 7 --- -/-	9, 10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

31 July 1998

Date of mailing of the international search report

07/08/1998

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Authorized officer

Fischer, B

# INTERNATIONAL SEARCH REPORT

b National Application No

PCT/GB 98/01205

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RULKE R E ET AL: "Insertion reactions involving palladium complexes with nitrogen ligands I. Reactivity towards carbon monoxide of methylpalladium(II) complexes containing bidentate alpha-diimine ligands: crystal structures of four methylpalladium (II) and acylpalladium(II) complexes" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 508, no. 1, 8 February 1996, page 109-120 XP004036213 see page 111, column 2	1-4,6
Y	see page 111, column 1, paragraph 2.1	9,10
X	ORRELL K G ET AL: "Stereochemically non-rigid transition metal complexes of 2,6 -bis'(1-phenylimino) ethyl!pyridine (BIP) Part 1. Dynamic NMR studies of 'M(C6F5)2(BIP)! (M = Pd or Pt)" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 530, no. 1-2, 1 March 1997, page 235-246 XP004064350 see abstract see page 236; figure 1 see page 237	1-3,5
X	DE FELICE V ET AL: "Cationic Platinum(II)- or Palladium(II)-carbyl complexes and unsaturated substrates: a facile way to C-C bond formation" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 493, no. 1, 17 May 1995, page i-11 XP004023993 see page 2; figure 1; examples 2-4 see example XXIII; table 2	1
A	CANOVESE L ET AL: "Mechanism of oxidative allyl transfer from allylic ammonium cations to palladium(0) alpha-diimine complexes" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 508, no. 1, 8 February 1996, page 101-108 XP004036212	1,3-5



# INTERNATIONAL SEARCH REPORT

Information on patent family members

I. National Application No

PCT/GB 98/01205

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU 6404096 A	05-02-1997
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		NO 976120 A	02-03-1998
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